

MEMBRANES WITH FLUID BARRIER PROPERTIES AND ARTICLES  
CONTAINING SUCH MEMBRANES

FIELD OF THE INVENTION

**[0001]** This invention concerns membranes including fillers suitable for applications that require both barrier properties and flexibility, particularly for use in preparing bladders for inflated objects and cushioning devices. The present invention further relates to articles that are inflated or have inflated elements.

BACKGROUND OF THE INVENTION

**[0002]** Barrier membranes and inflatable bladders formed from such membranes have been used in a variety of products for inflation or cushioning, including vehicle tires, balls, accumulators used on heavy machinery, and in footwear, especially athletic shoes. It is often desirable to use polymeric materials that are thermoplastic to form the membranes because thermoplastic materials may be reclaimed and reformed into new articles, thus reducing waste during manufacturing operations and promoting recycling after the useful life of an article. While thermoplastic barrier films may be flexed to a certain extent due to their thinness, thermoplastic barrier films having only barrier material layers generally do not have sufficient elasticity for many applications, particularly for applications in which the inflated bladder is subjected to high strains during use. In order to overcome this problem, the barrier materials have been blended or layered with elastomeric materials. Elastomeric materials, or elastomers, are able to substantially recover their original shape and size after removal of a deforming force, even when the part has undergone significant deformation.

Elastomeric properties are important in many inflatable bladder applications, including inflatable bladders for footwear, game balls, and hydraulic accumulators.

**[0003]** One key property of a membrane that forms an inflated bladder is that of its gas transmission rate, which quantifies its barrier effectiveness toward an inflating gas. An accepted method of measuring the relative permeance, permeability, and gas transmission rates of different film materials is set forth in the procedure designated as ASTM D-1434-82-V. It is desirable for the inflated bladder to retain a useful amount of internal pressure throughout its lifetime without the need to periodically re-introduce an inflating gas. Thus, the inflated bladder could be permanently sealed and would not need to be re-inflated. One way to achieve the lower gas transmission rate needed for such “permanently inflated” bladders would be to increase the thickness of the barrier material layer of the membrane used to form the bladder. However, because of the increased stiffness that would result from a thicker layer of the barrier material, this is not an attractive option. It would be preferred from the standpoint of maintaining membrane resiliency to reduce gas transmission rate by a method that does not substantially increase the stiffness of the membrane.

**[0004]** Styling is another concern in some applications for bladders, such as bladders for shoes or for play balls. Styling attracts the eye of the purchaser and makes the product appealing. One recent styling innovation for footwear is that of a transparent element with an external surface. It is often desirable for the transparent element to be crystal clear for a sharp, clean, “high-

tech" look. Inflated bladders, incorporated into footwear for cushioning, can also function as an element with transparency. The bladder must, however, maintain the elastomeric and gas barrier properties needed to fulfill its primary function of providing cushioning to the foot. Thus it would be desirable to reduce gas transmission rate through the membrane by a method that does not make a membrane that is opaque or hazy in appearance.

**[0005]** Membranes with layers of flexible materials and layers of fluid barrier materials are described, for example, in U.S. Patent No. 6,082,025, issued July 4, 2000; U.S. Patent No. 6,013,340, issued January 11, 2000; U.S. Patent No. 5,952,065, issued September 14, 1999; and U.S. Patent No. 5,713,141, issued February 3, 1998, each of which is incorporated herein by reference. While the membranes disclosed in these references provide flexible, "permanently" inflated, gas-filled bladders, further improvements in resiliency would be desirable.

**[0006]** Mica and other large aspect ratio platelet fillers have been employed to decrease the gas transmission rate of inflated membranes. Tokoh et al., U.S. Patent No. 5,221,566, teaches that a container may be made with a first layer containing 50-95% EVOH and 5-50% of an inorganic filler and a second layer of a moisture resistant thermoplastic resin such as polyolefin. The inorganic filler has an average flake diameter of not more than 50 microns, an aspect ratio of at least three, and a whiteness of at least 80 (measured with Kett spectrophotometer). The Tokoh et al. materials do not have the resiliency required for cushioning devices and many inflated articles.

**[0007]** Thus a need remains for flexible barrier material compositions that are highly impervious to the inflating gas.

#### SUMMARY OF THE INVENTION

**[0008]** The invention provides a membrane having at least one layer, with the membrane comprising at least one elastomeric material and at least one polymeric fluid barrier material, in which a laminar nano-filler having an average platelet thickness of up to about 10 nanometers and an average aspect ratio of at least about 200 is present in at least one of the membrane layers. The membrane preferably includes at least one elastomeric layer containing an elastomeric material and at least one barrier layer containing a polymeric fluid barrier material. The elastomeric material provides resiliency and dimensional stability to the membrane of the invention, while the polymeric fluid barrier material allows the membrane to prevent the transfer of a fluid from one side of the membrane to the other. The laminar nano-filler increases the ability of the membrane to prevent transfer of a fluid from one side of the membrane to the other without appreciably increasing the opacity or haziness of the membrane and without appreciably decreasing the resilience of the membrane.

**[0009]** Such durable, elastomeric barrier membranes may be used to prepare inflated bladders. By "durable" it is meant that the membrane has excellent resistance to fatigue failure, particularly that a membrane of the invention can undergo repeated flexing and/or deformation and recover without

delamination along the layer interfaces of the membranes, preferably over a broad range of temperatures.

**[0010]** For purposes of this invention, the term "membrane" is used to denote a free-standing film separating a fluid, particularly a gas, preferably at higher than atmospheric pressure, from another fluid (liquid or gas) or from the gas at a lower pressure. Films laminated or painted onto another article for purposes other than separating fluids are excluded from the present definition of a membrane.

**[0011]** In a further aspect, the invention provides a membrane that includes a layer of a microlayer polymeric composite that has microlayers of at least one polymeric fluid barrier material and microlayers of at least one elastomeric material, optionally layers of one or more further materials, all of the different layers being arranged in regular repeating order in the composite. The polymeric fluid barrier material and/or the elastomeric material layers further include a laminar nano-filler having an average platelet thickness of up to about 10 nanometers and aspect ratio of at least about 200.

**[0012]** The invention further provides enclosures formed from the membranes of the invention, including but not limited to permanently sealed, inflated bladders, as well as articles containing such enclosures and bladders. The bladder may be inflated with a gas such as nitrogen or air. The bladder may be used to inflate or cushion, for example to inflate a sports ball or to provide cushioning in footwear. The bladder may be combined with other materials, such as cloth or foam outer layers, in forming a cushioning device.

**[0013]** The barrier membrane preferably has a gas transmission rate that is sufficiently low to allow a sealed bladder to remain "permanently" inflated; that is, to retain a useful internal pressure for the useful life of the article into which it is incorporated. An accepted method for measuring the relative permeance, permeability, and diffusion of different film materials is ASTM D-1434-82-V. The gas transmission rate of a membrane is expressed as the quantity of gas per area per time that diffuses through the membrane. The gas transmission rate may be expressed in units of (cc)(mil)/(m<sup>2</sup>)(24 hours), at standard temperature and pressure. The gas transmission rate of the barrier membrane provided by the invention is preferably less than about 1 (cc)(20 mils)/(m<sup>2</sup>)(24 hours).

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0014]** The present invention will become more fully understood from the detailed description and the accompanying drawing, wherein:

**[0015]** Figure 1 shows a multilayer membrane of the invention;

**[0016]** Figure 2 shows a multilayer membrane of the invention including a microlayer polymeric composite layer; and

**[0017]** Figure 3 shows an expanded view of a section of the multilayer membrane of Figure 2.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0018]** The following description of the preferred embodiment(s) is merely exemplary in nature and is in no way intended to limit the invention, its application, or uses.

**[0019]** The invention provides a membrane having at least one layer, with the membrane comprising at least one elastomeric material and at least one polymeric fluid barrier material, in which a laminar nano-filler having an average platelet thickness of up to about 10 nanometers and an average aspect ratio of at least about 200 is present in at least one of the membrane layers. The membrane may be a single layer containing the elastomeric material, the fluid barrier material, and the laminar nano-filler, but the membrane preferably contains at least two layers. The membrane preferably includes at least one layer of an elastomeric material and at least one layer of a polymeric barrier material, in which the elastomeric material layer and/or the polymeric barrier material layer comprises the laminar nano-filler having an average platelet thickness of up to about 10 nanometers and aspect ratio of at least about 200. Preferably, the laminar nano-filler is combined with the fluid barrier material, e.g. in islets of the fluid barrier material in a single layer membrane or in the fluid barrier material layer(s) of a multi-layer membrane.

**[0020]** The elastomeric material may be a thermoplastic elastomer or rubber. Thermoplastic elastomers in general have a soft or flexible segment or segments that provide elastomeric properties and hard or rigid segments acting as thermally reversible physical crosslinks that enable the polymer to be

processed as a thermoplastic material while retaining elastic behavior at room temperature. For example, one kind of thermoplastic elastomer has one or more soft or rubbery polymer segments, such as a polyester or polyether segments, and hard or glassy polymer segments, such as polyurethane or polyurea segments. A-B-A block copolymers such as styrene/butadiene/styrene block copolymers have a similar structure, but the center of the polymer chain is always the soft or elastic segment (e.g., rubbery polybutadiene) while the ends are glassy (e.g., polystyrene). Another suitable class of thermoplastic elastomers are dynamic vulcanizates, in which a rubbery phase is vulcanized in a molten thermoplastic phase under shear. Particular examples of elastomeric materials suitable for forming elastomeric layers include, without limitation, polyurethane elastomers, including elastomers based on both aromatic and aliphatic isocyanates; flexible polyolefins, including flexible polyethylene and polypropylene homopolymers and copolymers; styrenic thermoplastic elastomers, including styrene (ethylene-butylene) styrene block copolymer; polyamide elastomers; polyamide-ether elastomers; ester-ether and ester-ester elastomers; flexible ionomers; thermoplastic vulcanizates; flexible poly(vinyl chloride) homopolymers and copolymers; flexible acrylic polymers; and blends and alloys of these, such as poly(vinyl chloride) alloys like poly(vinyl chloride)-polyurethane alloys. Rubbers that may be extruded before crosslinking may also be used, with the crosslinking being carried out after extrusion of the membrane. Examples of rubbers include, without limitation nitrile rubber and butyl rubber.



The different elastomeric materials may be combined as blends in a layer or may be included as separate layers of the membrane.

**[0021]** Particularly suitable are thermoplastic polyester-polyurethanes, polyether-polyurethanes, and polycarbonate-polyurethanes, including, without limitation, polyurethanes polymerized using as diol reactants polytetrahydrofurans, polyesters, polylactone polyesters (especially polycaprolactone diols) or polyesters prepared from monocarboxylic acids containing an hydroxyl group, and polyethers of ethylene oxide, propylene oxide, and copolymers including ethylene oxide and propylene oxide. These polymeric diol-based polyurethanes are prepared by reaction of the polymeric diol (polyester diol, polyether diol, polycaprolactone diol, polytetrahydrofuran diol, or polycarbonate diol), one or more polyisocyanates, and, optionally, one or more chain extension compounds. Chain extension compounds, as the term is used herein, are compounds having two or more functional groups, preferably two functional groups, reactive with isocyanate groups. Preferably the polymeric diol-based polyurethane is substantially linear (i.e., substantially all of the reactants are di-functional).

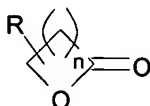
**[0022]** The polyester diols used in forming the preferred thermoplastic polyurethanes of the invention are in general prepared by the condensation polymerization of polyacid compounds (including anhydrides and esters thereof) and polyol compounds. Preferably, the polyacid compounds and polyol compounds are di-functional, i.e., diacid compounds (including anhydrides of diacid compounds) and diols are used to prepare substantially linear polyester

diols, although minor amounts of mono-functional, tri-functional, and higher functionality materials (perhaps up to 5 mole percent) can be included. Suitable dicarboxylic acids include, without limitation, glutaric acid, succinic acid, malonic acid, oxalic acid, phthalic acid, hexahydrophthalic acid, adipic acid, maleic acid, anhydrides of these, and mixtures thereof. Suitable polyols include, without limitation, wherein the extender is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, cyclohexanedimethanol, 2-ethyl-1,6-hexanediol, 1,4-butanediol, 1,5-pentanediol, 1,3-propanediol, butylene glycol, neopentyl glycol, and combinations thereof. Small amounts of triols or higher functionality polyols, such as trimethylolpropane or pentaerythritol, are sometimes included. In a preferred embodiment, the carboxylic acid includes adipic acid and the diol includes 1,4-butanediol. Typical catalysts for the esterification polymerization are protonic acids, Lewis acids, titanium alkoxides, and dialkyl tin oxides.

**[0023]** Polymerization of an hydroxy carboxylic acid compound will also produce a polyester. Such a reaction may be carried out with or without an initiating polyol.

**[0024]** Polyether or polylactone diol reactants may also be used in preparing preferred thermoplastic polyurethanes. The polyether or polylactone diols may be prepared by reacting a diol initiator, e.g., a diol such as ethylene or propylene glycol, with a lactone or alkylene oxide or other oxirane chain-extension reagent. Suitable chain-extension reagents for preparing polylactones

are lactones that can be ring opened by an active hydrogen. Examples of suitable lactones include, without limitation,  $\epsilon$ -caprolactone,  $\gamma$ -caprolactone,  $\beta$ -butyrolactone,  $\beta$ -propiolactone,  $\gamma$ -butyrolactone,  $\alpha$ -methyl- $\gamma$ -butyrolactone,  $\beta$ -methyl- $\gamma$ -butyrolactone,  $\gamma$ -valerolactone,  $\delta$ -valerolactone,  $\gamma$ -decanolactone,  $\delta$ -decanolactone,  $\gamma$ -nonanoic lactone,  $\gamma$ -octanoic lactone, and combinations of these. In one preferred embodiment, the lactone is  $\epsilon$ -caprolactone. Lactones useful in the practice of the invention can also be characterized by the formula:

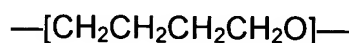


wherein  $n$  is a positive integer of 1 to 7 and  $R$  is one or more H atoms, or substituted or unsubstituted alkyl groups of 1-7 carbon atoms. Useful catalysts include, those mentioned above for polyester synthesis. Alternatively, the reaction can be initiated by forming a sodium salt of the hydroxyl group on the molecules that will react with the lactone ring.

**[0025]** In another embodiment of the invention, a diol initiator is reacted with an oxirane-containing compound to produce a polyether diol to be used in the polyurethane polymerization. The oxirane-containing compound is preferably an alkylene oxide or cyclic ether, especially preferably a compound selected from ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, and combinations of these. Alkylene oxide polymer segments include, without limitation, the polymerization products of ethylene oxide, propylene oxide, 1,2-cyclohexene oxide, 1-butene oxide, 2-butene oxide, 1-hexene oxide, tert-butylethylene oxide, phenyl glycidyl ether, 1-decene oxide, isobutylene oxide,

cyclopentene oxide, 1-pentene oxide, and combinations of these. Ethylene oxide, propylene oxide, and combinations of these are particularly preferred. The alkylene oxide polymerization is typically base-catalyzed. The polymerization may be carried out, for example, by charging the hydroxyl-functional initiator and a catalytic amount of caustic, such as potassium hydroxide, sodium methoxide, or potassium tert-butoxide, and adding the alkylene oxide at a sufficient rate to keep the monomer available for reaction. Two or more different alkylene oxide monomers may be randomly copolymerized by coincidental addition and polymerized in blocks by sequential addition. Homopolymers or copolymers of ethylene oxide or propylene oxide are preferred.

**[0026]** Tetrahydrofuran polymerizes under known conditions to form repeating units



Tetrahydrofuran is polymerized by a cationic ring-opening reaction using such counterions as  $\text{SbF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{SbCl}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{FSO}_3^-$ , and  $\text{ClO}_4^-$ . Initiation is by formation of a tertiary oxonium ion. The polytetrahydrofuran segment can be prepared as a “living polymer” and terminated by reaction with the hydroxyl group of a diol such as any of those mentioned above.

**[0027]** Aliphatic polycarbonate diols are prepared by the reaction of diols with dialkyl carbonates (such as diethyl carbonate), diphenyl carbonate, or dioxolanones (such as cyclic carbonates having five- and six-member rings) in the presence of catalysts like alkali metal, tin catalysts, or titanium compounds. Useful diols include, without limitation, any of those already mentioned. Aromatic

polycarbonates are usually prepared from reaction of bisphenols, e.g., bisphenol A, with phosgene or diphenyl carbonate.

**[0028]** The polymeric diol, such as the polymeric polyester diols described above, that are used in the polyurethane synthesis preferably have a number average molecular weight (determined for example by the ASTM D-4274 method) of from about 300 to about 4,000; more preferably from about 400 to about 3,000; and still more preferably from about 500 to about 2,000. The polymeric diol generally forms a "soft segment" of the elastomeric polyurethane.

**[0029]** The synthesis of the elastomeric polyurethane may be carried out by reacting one or more of the above polymeric diols, one or more compounds having at least two isocyanate groups, and, optionally, one or more chain extension agents. The elastomeric polyurethanes are preferably linear and thus the polyisocyanate component preferably is substantially di-functional. Useful diisocyanate compounds used to prepare the thermoplastic polyurethanes of the invention, include, without limitation, isophorone diisocyanate (IPDI), methylene bis-4-cyclohexyl isocyanate, cyclohexylene diisocyanate (CHDI), m-tetramethyl xylylene diisocyanate (m-TMXDI), p-tetramethyl xylylene diisocyanate (p-TMXDI), ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane (hexamethylene diisocyanate or HDI), 1,4-butylene diisocyanate, lysine diisocyanate, 1,4-methylene bis-(cyclohexyl isocyanate), the various isomers of toluene diisocyanate, meta-xylylenediisocyanate and para-xylylenediisocyanate, 4-chloro-1,3-phenylene diisocyanate, 1,5-tetrahydro-naphthalene diisocyanate, 4,4'-dibenzyl diisocyanate, and 1,2,4-benzene

triisocyanate, xylylene diisocyanate (XDI), and combinations thereof. Particularly useful is diphenylmethane diisocyanate (MDI).

**[0030]** Useful active hydrogen-containing chain extension agents generally contain at least two active hydrogen groups, for example, diols, dithiols, diamines, or compounds having a mixture of hydroxyl, thiol, and amine groups, such as alkanolamines, aminoalkyl mercaptans, and hydroxyalkyl mercaptans, among others. The molecular weight of the chain extenders preferably range from about 60 to about 400. Alcohols and amines are preferred. Typical examples of useful diols that are used as polyurethane chain extenders include, without limitation, 1,6-hexanediol, cyclohexanedimethanol (sold as CHDM by Eastman Chemical Co.), 2-ethyl-1,6-hexanediol, Esterdiol 204 (sold by Eastman Chemical Co.), 1,4-butanediol, ethylene glycol and lower oligomers of ethylene glycol including diethylene glycol, triethylene glycol and tetraethylene glycol; propylene glycol and lower oligomers of propylene glycol including dipropylene glycol, tripropylene glycol and tetrapropylene glycol; 1,3-propanediol, 1,4-butanediol, neopentyl glycol, dihydroxyalkylated aromatic compounds such as the bis (2-hydroxyethyl) ethers of hydroquinone and resorcinol; p-xylene- $\alpha,\alpha'$ -diol; the bis (2-hydroxyethyl) ether of p-xylene- $\alpha,\alpha'$ -diol; m-xylene- $\alpha,\alpha'$ -diol and the bis (2-hydroxyethyl) ether and mixtures thereof. Suitable diamine extenders include, without limitation, p-phenylenediamine, m-phenylenediamine, benzidine, 4,4'-methylenedianiline, 4,4'-methylenibis (2-chloroaniline), ethylene diamine, and combinations of these. Other typical chain extenders are amino alcohols such as ethanolamine, propanolamine, butanolamine, and combinations of these.

Preferred extenders include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, and combinations of these.

**[0031]** In addition to the above-described di-functional extenders, a small amount of tri-functional extenders such as trimethylolpropane, 1,2,6-hexanetriol and glycerol, and/or mono-functional active hydrogen compounds such as butanol or dimethyl amine, may also be present. The amount of tri-functional extenders and/or mono-functional compounds employed would preferably be 5.0 equivalent percent or less based on the total weight of the reaction product and active hydrogen containing groups employed.

**[0032]** The reaction of the polyisocyanate(s), polymeric diol(s), and, optionally, chain extension agent(s) is typically conducted by heating the components, for example by melt reaction in a twin screw extruder. Typical catalysts for this reaction include organotin catalysts such as stannous octoate or dibutyl tin dilaurate. Generally, the ratio of polymeric diol, such as polyester diol, to extender can be varied within a relatively wide range depending largely on the desired hardness of the final polyurethane elastomer. For example, the equivalent proportion of polyester diol to extender may be within the range of 1:0 to 1:12 and, more preferably, from 1:1 to 1:8. Preferably, the diisocyanate(s) employed are proportioned such that the overall ratio of equivalents of isocyanate to equivalents of active hydrogen containing materials is within the range of 0.95:1 to 1.10:1, and more preferably, 0.98:1 to 1.04:1. The polymeric diol segments typically are from

about 35% to about 65% by weight of the polyurethane polymer, and preferably from about 35% to about 50% by weight of the polyurethane polymer.

**[0033]** It may be desirable in certain applications to include blends of polyurethanes in the elastomeric layer or layers of the membrane, such as when susceptibility to hydrolysis is of particular concern. For example, a polyurethane including soft segments of polyether diol or polyester diol wherein the repeating units of the reaction product has more than eight carbon atoms can be blended with a polyurethane including polyester diol having repeating units of eight or fewer carbon atoms or products of branched diols. Preferably, the polyurethanes other than those including polyester diol repeating units having eight or fewer carbon atoms or with oxygen atoms connected to tertiary carbons will be present in the blends in an amount up to about 30 wt.%, (i.e. 70.0 wt.% polyethylene glycol adipate based polyurethane 30.0% isophthalate polyester diol based polyurethane). Specific examples of the polyester diols wherein the reaction product has more than eight carbon atoms include poly(ethylene glycol isophthalate), poly(1,4-butanediol isophthalate) and poly(1,6-hexanediol isophthalate).

**[0034]** Instead of blends of various thermoplastic polyurethanes, a single polyurethane having various soft segments may be used. In one embodiment, the soft segments may include soft segments of polyester or polyether polyol having repeating units with a total of eight or fewer carbon atoms combined with soft segments of polyester or polyether polyol having repeating units with a total of more than eight carbon atoms. It is preferred that the total amount of soft segment



having repeating units with a total carbon atom count of more than eight be present in an amount of up to about 30 wt.% of the total weight of soft segments included in the polyurethane. One preferred embodiment includes at least about 70 wt.% of the soft segment with repeating units having eight or fewer carbon atoms.

**[0035]** Specific examples of suitable commercial elastomeric materials include polyamide-ether elastomers marketed under the trademark PEBAX® by Elf Atochem, ester-ether elastomers marketed under the trademark HYTREL® by DuPont, ester-ester and ester-ether elastomers marketed under the trademark ARNITEL® by DSM Engineering, thermoplastic vulcanizates marketed under the trademark SANTOPRENE® by Advanced Elastomeric Systems, elastomeric polyamides marketed under the trademark GRILAMID® by EMS-Chemie, Sumter, SC, and elastomeric polyurethanes marketed under the trademark PELLETHANE® by Dow Chemical Company, Midland, MI, ELASTOLLAN® polyurethanes marketed by BASF Corporation, Mt. Olive, NJ, TEXIN® and DESMOPAN® polyurethanes marketed by Bayer, MORTHANE® polyurethanes marketed by Huntsman, and ESTANE® polyurethanes marketed by Noveon.

**[0036]** The membrane also includes a polymeric barrier material. The polymeric barrier material may be blended with the elastomer material, for example to form a single-layer membrane or as one layer of a multi-layer membrane. In this case, the polymeric barrier layer material is preferably present in a minor amount and the elastomer material in a major amount, so that the elastomer material is a continuous matrix.

**[0037]** The polymeric barrier material, however, is preferably in at least one layer separate from a layer containing the elastomeric material. In general, the polymeric barrier material layers will be thinner than the elastomeric material layers so that the membrane will be flexible and durable.

**[0038]** Suitable polymeric fluid barrier materials include, without limitation, ethylene-vinyl alcohol copolymers; poly(vinyl chloride); polyvinylidene polymers and copolymers, including polyvinylidene chloride; polyamides including amorphous polyamides; acrylonitrile polymers, including acrylonitrile-methyl acrylate copolymers; polyurethane engineering plastics; poly(methyl pentene) resins; ethylene-carbon monoxide copolymers; liquid crystal polymers; polyesters such as polyethylene terephthalate; polyimides, including polyether imides and polyacrylic imides; and other such polymeric materials known to have relatively low gas transmission rates. Blends and grafts of these materials, such as combinations of polyimides and crystalline polymers such as liquid crystal polymers, polyamides and polyethylene terephthalate, and combinations of polyamides with styrenics, are also suitable. The membrane may have a layer or layers with combinations of different fluid barrier materials, or the different fluid barrier materials may also be included as separate layers of the membrane.

**[0039]** Ethylene-vinyl alcohol copolymers are preferred, particularly those copolymers in which the ethylene comonomer unit content is from about 25 mole percent to about 50 mole percent, and more particularly from about 25 mole percent to about 40 mole percent. Ethylene-vinyl alcohol copolymers are prepared by hydrolyzing ethylene-vinyl acetate copolymers, as is well-known.

**[0040]** Examples of suitable specific commercial products include acrylonitrile copolymers such as BAREX<sup>®</sup>, available from BP Chemicals, Inc.; polyurethane engineering plastics such as ISOPLAST<sup>®</sup>, available from Dow Chemical Corp., Midland, MI; ethylene vinyl alcohol copolymers marketed under the trademarks EVAL<sup>®</sup> by EVAL Company of America (EVALCA), Lisle, Illinois, SOARNOL<sup>®</sup> by Nippon Goshei Co., Ltd. (U.S.A.) of New York, NY, CLARENE<sup>®</sup> by Solvay, and SELAR<sup>®</sup> OH by DuPont; polyvinylidene chloride available from Dow Chemical under the tradename SARAN<sup>®</sup>, and from Solvay under the tradename IXAN<sup>®</sup>; liquid crystal polymers such as VECTRA<sup>®</sup> from Hoechst Celanese and XYDAR<sup>®</sup> from Amoco Chemicals; MXD6 nylon, available from Mitsubishi Gas Chemical Co., Ltd, Solvay, and Toyobo and amorphous nylons such as NOVAMID<sup>®</sup> X21 from Mitsubishi, SELAR<sup>®</sup> PA from DuPont, and GELON A-100 from General Electric Company; KAMAX<sup>®</sup> polyacrylic-imide copolymer available from Rohm & Haas; polyetherimides sold under the tradename ULTEM<sup>®</sup> by General Electric; VINEX poly(vinyl alcohol) available from Air Products; and polymethylpentene resins available from Phillips 66 Company under the tradename CRYSTALOR and from Mitsui Petrochemical Industries under the tradename TPX<sup>®</sup>. Highly preferred commercially available copolymers of ethylene and vinyl alcohol, such as those available from EVALCA, will typically have an average ethylene content of between about 25 mol% to about 48 mol%.

**[0041]** At least one layer of the membrane, or at least one polymeric material of a single-layer membrane, contains a laminar nano-filler having an average platelet thickness of up to about 10 nanometers and an aspect ratio of at

least about 200. In the preferred membrane containing an elastomeric layer and a barrier material layer, the elastomeric layer, the barrier material layer, or both include a laminar nano-filler having an average platelet thickness of up to about 10 nanometers and an aspect ratio of at least about 200. Preferred laminar nano-fillers have a thickness of from about 1 nm to about 10 nm and height and width each independently from about 0.1 micron to about 1.5 microns. The aspect ratio is preferably from about 200 to about 1000 and more preferably from about 200 to about 500. One preferred laminar nano-filler is a montmorillonite clay.

**[0042]** In another preferred membrane, a single layer includes a thermoplastic material, such as nitrile rubber or thermoplastic polyurethane elastomer, in a major amount, a gas barrier polymeric material, such as a polyamide, in a minor amount, and the laminar nano-filler in an amount of up to about 10% by weight of the total composition. In one preferred embodiment, the elastomer is a dynamic vulcanizate rubber in a thermoplastic material, such as in another elastomer or in the polymeric barrier material. Covalent bonding between the rubber and the polymeric barrier material or the other thermoplastic elastomer may be used to promote good interfacial adhesion.

**[0043]** The laminar nano-fillers may be used with hydrophilic polymers without modification or preferably may be modified to increase their affinity for the polymer (e.g., to aid in exfoliating and dispersing the nano-fillers) or to help prevent re-agglomeration. In one preferred modification octadecyl trimethyl ammonium chloride or bromide is mixed with a clay laminar nano-filler to replace

sodium ions initially on the surface of the clay. In general, a laminar nano-filler may be surface-modified by wetting the nano-filler, adding the treating material, and then drying the nano-filler.

**[0044]** The laminar nano-fillers have advantageous properties when used in the membranes. First, the laminar nano-fillers improve gas barrier properties of the membrane at a loading (e.g., about 4 to about 10 weight percent ) that does not substantially affect the clarity of the membrane, while use of traditional fillers such as talc or mica will cause an increase in haze or opacity at levels high enough to affect the gas transmission rate of the membrane. In addition, the lower loading levels and smaller flakes of the laminar nano-fillers improve modulus and toughness of the membranes compared to membranes made with traditional fillers. Incorporating the laminar nano-filler into the polymeric barrier material appears in at least some cases to promote crystallization of the polymeric barrier material. Incorporating the laminar nano-filler into the elastomeric material can provide gas barrier properties to a layer that essentially does not contribute to the gas barrier property of the membrane without the laminar nano-filler.

**[0045]** The laminar nano-filler may be incorporated into the layer material, for example, by well-known compounding methods. Alternatively, the laminar nano-filler may be incorporated by combining the laminar nano-filler with a monomer or other reactant used to form the polymer before polymerization.. As mentioned, the laminar nano-filler may be treated with a compatibilizing agent to aid in their dispersion in the layer material.

**[0046]** Additional materials that may be in one or more of the layers include modifiers and other additives, preferably in minor amount. Examples of such modifiers and additives include, without limitation, plasticizers, light stabilizers, hydrolytic stabilizers, thermal stabilizers, brighteners, antioxidants, rheology modifiers, organic anti-block compounds, fungicides, antimicrobials (including bacteriocides and the like), mold release agents, waxes such as Montan esters or bis-amide waxes, processing aids, and combinations of these. Tinted transparent membranes may be formed with transparent colorants, such as dyes or transparent pigments. Special effects in the transparent membrane, e.g. iridescence, may be achieved by using special effect pigments.

**[0047]** Examples of hydrolytic stabilizers include two commercially available carbodiimide based hydrolytic stabilizers known as STABAXOL P and STABAXOL P-100, which are available from Rhein Chemie of Trenton, New Jersey. Other carbodiimide- or polycarbodiimide-based hydrolytic stabilizers or stabilizers based on epoxidized soy bean oil may be useful. The total amount of hydrolytic stabilizer employed will generally be less than 5.0 wt.% of the total weight of the layer.

**[0048]** Plasticizers can be included for purposes of increasing the flexibility and durability of the final product as well as facilitating the processing of the material from a resinous form to a membrane or sheet. By way of example, and without intending to be limiting, plasticizers such as those based on butyl benzyl phthalate (which is commercially available, e.g. as Santicizer 160 from Monsanto) have proven to be particularly useful. Regardless of the plasticizer or

mixture of plasticizers employed, the total amount of plasticizer, if any, should generally be less than 20.0 wt.% of the total layer, preferably less than about 5% by weight of the total layer.

**[0049]** The membrane of the invention may include a layer of a microlayer polymeric composite. A microlayer polymeric composite layer has alternating microlayers of at least one fluid barrier material, as described above, and at least one elastomeric material, as described above. Also contemplated are microlayer polymeric composite layers that include microlayers of different fluid barrier materials and/or microlayers of different elastomeric materials, the different layers being arranged in regular repeating order. Other layers in addition to elastomeric layers and fluid barrier layers that alternate along with them in a regular, repeating order may optionally be included. The microlayer polymeric composite layer should have at least about 10 microlayers. Preferably, the microlayer polymeric composite layer has at least about 20 microlayers, more preferably at least about 30 microlayers, and still more preferably at least about 50 microlayers. The microlayer polymeric composite layer can have thousands of microlayers, and the skilled artisan will appreciate that the number of microlayers will depend upon such factors as the particular materials chosen, thicknesses of each layer, the thickness of the microlayer polymeric composite layer, the processing conditions for preparing the multilayers, and the final application of the composite. The microlayer polymeric composite layer preferably has from about 10 to about 1000 microlayers, more preferably from

about 30 to about 1000 and even more preferably it has from about 50 to about 500 microlayers.

**[0050]** In the microlayer polymeric composite layer, the average thickness of each individual microlayer of the fluid barrier material may be as low as a few nanometers to as high as several mils (about 100 microns) thick. Preferably, the individual microlayers have an average thickness of up to about 0.1 mil (about 2.5 microns). Average thicknesses of about 0.0004 mil (about 0.01 micron) to about 0.1 mil (about 2.5 microns) are particularly preferable. For example, the individual barrier material microlayers can be, on average, about 0.05 mils (about 1.2 microns). Having thinner microlayers of the fluid barrier material improves the ductility of the membrane. The microlayer polymeric composite layer is preferably on average from about 0.25 mil (about 6.35 microns) to about 102 mils (2600 microns) thick, more preferably on average from about 3 mils (about 75 microns) to about 200 mils (about 0.5 cm) thick, even more preferably from about 3 mils (about 75 microns) to about 40 mils (about 0.1 cm).

**[0051]** The alternating layers of the structural polymer and the fluid barrier polymer have their major surfaces aligned substantially parallel to the major surfaces of the composite. There are a sufficient number of layers of the fluid barrier polymer so that the microlayer composite has the desired fluid transmission rate.

**[0052]** The microlayer polymeric composite layer may be formed by using a two-layer, three-layer, or five-layer feed block that directs the layered



stream into a static mixer or layer multiplier. The static mixer has multiple mixing elements, preferably at least about five elements, that increases the number of layers geometrically. A preferred method for forming the microlayer polymeric composite layer is described in detail in Schrenk, et al., U.S. Patent No. 5,094,793, issued March 10, 1992, which is incorporated herein in its entirety by reference. Protective boundary layers may be incorporated according to the method of Ramanathan et al., U.S. Patent No. 5,269,995, issued December 14, 1993, which is incorporated herein in its entirety by reference. The protective layers protect the elastomer and fluid barrier layers from instability and breakup during the layer formation and multiplication. The protective layers are provided by a stream of molten thermoplastic material which is supplied to the exterior surfaces of the composite stream to form a protective boundary layer at the wall of the coextrusion apparatus. The protective layer may add special optical or physical attributes to the microlayer polymeric composite material, such as special coloration, including metallic coloration obtained by including metallic or other flake pigments in the protective boundary layer.

**[0053]** Although it is not necessary for all of the microlayers to be complete layers, that is to extend in the plane of that microlayer to all edges of the membrane, it is desirable for most microlayers to be substantially complete layers, that is to extend to the edges of the membrane.

**[0054]** The membrane having the elastomeric material, fluid barrier material, and nano-filler may be formed into a sealed, inflated bladder. The

membrane may be of any convenient length and width for forming the desired inflated bladder.

**[0055]** The membrane of the invention can include the microlayer polymeric material as one or more layers. Any number of microlayer layers, preferably from one to about 5, more preferably one to three can be used as layers of the membrane. The membrane preferably includes at least one further layer that is a layer of an elastomer, preferably a thermoplastic polyurethane. One preferred membrane of the invention includes at least one layer A of an elastomeric polyurethane and at least one layer B of the microlayer polymeric composite. More preferably the membrane has layers A-B-A or layers A-B-A-B-A. In another embodiment, the membrane also contains layers C containing a blend of materials that include at least a thermoplastic polyurethane elastomer and a barrier material, such as ethylene-vinyl alcohol copolymer. The membrane layers may be arranged as C-A-B-A-C or A-C-A-B-A-C-A.

**[0056]** It is especially beneficial to include the laminar nano-filler of the invention in one or more of the materials used to make the microlayers of the microlayer polymeric composite. The process of forming the microlayers tends to align the nano-filler generally parallel to the faces of the microlayer polymeric composite. For a given amount of nano-filler in a membrane, the gas transmission rate is less in the case where the nano-filler is more parallel to the face of the membrane. The method of forming a microlayer polymeric composite membrane or layer of a membrane promote the desired generally parallel arrangement of the nano-filler relative to the face of the membrane.

**[0057]** One further feature of some of the membranes of the present invention is an enhanced bonding that can occur between layers of elastomeric material and fluid barrier material of the membrane or of a microlayer polymeric composite layer of the membrane. This enhanced bonding is generally accomplished by using materials for adjacent layers that have available functional groups that can participate in hydrogen bonding such as hydrogen atoms in hydroxyl groups or hydrogen atoms attached to nitrogen atoms in polyurethane groups that can hydrogen bond with various receptor groups such as oxygen atoms in hydroxyl groups, carbonyl oxygens in polyurethane groups and ester groups, and chlorine atoms in PVDC, for example. For example, hydrogen bonding is believed to occur when the elastomeric material comprises a polyester diol based polyurethane and the fluid barrier material includes a polymer selected from the group consisting of copolymers of ethylene and vinyl alcohol, polyvinylidene chloride, copolymers of acrylonitrile and methyl acrylate, polyethylene terephthalate, aliphatic and aromatic polyamides, crystalline polymers and polyurethane engineering thermoplastics. In addition to the hydrogen bonding, there may be a certain amount of covalent bonding between the layers. Still other factors such as orientation forces and induction forces, otherwise known as van der Waals forces, which result from London forces existing between any two molecules and dipole-dipole forces which are present between polar molecules are believed to contribute to the bond strength between contiguous layers. Besides the physical forces and chemical bonds, the interfacial structure also contributes significantly to the bond strength.

**[0058]** Referring now to the figures, Figure 1 shows membrane 10 having layers 12, 14, 18, and 20 of elastomeric material and layer 16 of polymeric fluid barrier material. Layers 12 and 20 are thicker, e.g. 12-14 mils, having polymeric material composed predominantly of polymeric elastomer, e.g. thermoplastic polyurethane elastomer, but which may include small amounts of other polymeric materials, such as the polymeric fluid barrier material of layer 16. Layers 14 and 18 are thinner, e.g. 1-3 mils, and functions as tie layers between outer layers 12 and 20 and the inner, barrier layer 16. The polymeric material of layers 14 and 18, for instance, consists essentially of thermoplastic polyurethane elastomer. The thermoplastic polyurethane elastomer can hydrogen bond with the material of polymeric fluid barrier material of layer 16, which is preferably an ethylene-vinyl alcohol copolymer. Hydrogen bonding takes place between the urethane groups of the polyurethane and the alcohol groups of the ethylene-vinyl alcohol copolymer. At least one of the layers contains the laminar nano-filler, preferably layer 16.

**[0059]** Figure 2 illustrates a membrane 110 having as a core, barrier layer a microlayer polymeric composite layer 124. Microlayer polymeric composite layer 124 may be 5-7 mils thick and has alternating layers of a polymeric barrier layer material and an elastomer material. Layers 112 and 120 may be, e.g. 25-27 mils, with polymeric material composed predominantly of polymeric elastomer, e.g. thermoplastic polyurethane elastomer, but which may include small amounts of other polymeric materials, such as a polymeric fluid barrier material. Layers 114 and 118 are thinner, e.g. 1-3 mils, with polymeric

material consisting essentially of thermoplastic polyurethane elastomer. The membrane 110 has outer skin layer 122 and 126, 1 to 2 mils thick, with polymeric material that also consists essentially of thermoplastic polyurethane elastomer. At least one of the layers contains the laminar nano-filler. Preferably, the laminar nano-filler is included in one or more of layers 112, 124, and 120.

**[0060]** Figure 3 shows an expanded view of a section of the multilayer membrane of Figure 2. A portion of layer 114 borders a portion of microlayer polymeric composite layer 124. Microlayer polymeric composite layer is shown with alternating thinner layers containing a polymeric fluid barrier material, preferably a copolymer of ethylene and vinyl alcohol, such as layer 140, and thicker layers of elastomer material, preferably thermoplastic polyurethane elastomer, such as layer 142. The laminar nano-filler may be included in both kinds of layers, but preferably the laminar nano-filler is included in at least the polymeric fluid barrier material layers.

**[0061]** The invention further provides bladders, especially inflated bladders, prepared from the membranes of the invention and articles including such bladders. The membranes of the invention offer flexibility and resistance to undesirable transmission of fluids such as an inflationary gas. These membranes can be inflated with a gas such as nitrogen and preferably provide a gas transmission rate value of about 10 cubic centimeters per square meter per atmosphere per day ( $\text{cc}/\text{m}^2 \cdot \text{atm} \cdot \text{day}$ ) or less. The durable, elastomeric membranes of the inflated bladders can be used in many applications, particularly for inflation or cushioning applications. By “durable” it is meant that

the membrane has excellent resistance to fatigue failure, which means that the membrane can undergo repeated flexing and/or deformation and recover without cracking or other failures, preferably over a broad range of environmental conditions such as temperature and relative humidity. For purposes of this invention, the term "membrane" is used to denote a free-standing film separating one fluid (whether gas or liquid) from another fluid. Films laminated or painted onto another article for purposes other than separating fluids are excluded from the present definition of a membrane.

**[0062]** While the membrane may be thin or thick, the membrane should be thick enough to provide adequate wall strength and yet thin enough to provide adequate flexibility. Membrane thicknesses are preferably from about 20 mils to about 70 mils, more preferably from about 20 mils to about 40 mils thick. In a preferred five-layer structure, it is desirable for a central fluid barrier material layer and for elastomeric material layers adjacent on either side of the fluid barrier layer to individually be at least about 0.4 mil thick, preferably at least about 0.5 mil thick, more preferably at least about 0.6 mil thick, and still more preferably at least about 1 mil thick, and up to about 3 mils thick, preferably up to about 2.5 mils thick, more preferably up to about 2 mils thick, and yet more preferably up to about 1.6 mils thick. The outermost layers are preferably blend layers of predominantly elastomeric material with a minor amount of fluid barrier material that are preferably at least about 7 mils thick, more preferably at least about 8 mils thick, and still more preferably at least about 9 mils thick; and preferably up to about 20 mils thick, more preferably up to about 15 mils thick.

**[0063]** In particular, the present invention provides an inflatable bladder for applications such as footwear, hydraulic accumulators, or for inflating objects such as sports balls, the bladder having a membrane that includes at least one elastomeric material and at least one polymeric fluid barrier material, preferably in separate layers, in which a laminar nano-filler having an average platelet thickness of up to about 10 nanometers and an average aspect ratio of at least about 200 is present in at least one of the membrane layers. The membrane of the invention has elastomeric mechanical properties that allows it to repeatedly and reliably absorb high forces during use without degradation or fatigue failure. It is particularly important in these kinds of applications for the membrane to have excellent stability in cyclic loading. The barrier membrane has a low gas transmission rate that allows it to remain inflated, and thus to provide cushioning or inflation, for substantially the expected life of the article without the need to periodically re-inflate and re-pressurize the bladder; thus it is permanently sealed.

**[0064]** A bladder may be produced by RF (radio frequency) welding two sheets of the microlayer material or microlayer-containing membrane, particularly when one layer is a polar material such as a polyurethane. Nonpolar materials such as polyolefins can be welded using ultrasound or heat sealing techniques. Other well-known welding techniques may also be employed.

**[0065]** The membrane may be formed into a bladder by a blow molding process. In general, the bladders may be formed by a first step of coextruding the layers, or plies, in a membrane of flat or tubular shape, then blow molding the

flat membrane or tube into a desired final shape. For example, melt materials of the layers may be co-extruded as a parison. A mold having the desired overall shape and configuration of the bladder is in position to receive the parison and is closed around the parison. The parison is cut at the edge of the mold. The mold is moved back to a position away from the extrusion die. The open portion of the parison above the mold is then fitted with a blow tube through which pressurized air or other gas, such as nitrogen, is provided. The pressurized air forces the parison against the inner surfaces of the mold. The material is hardened in the mold to form a bladder having the preferred shape and configuration. The blown, shaped membrane is allowed to cool and harden in the mold, which may be at about 30°F to 80°F, before it is removed from the mold. Meanwhile, a new mold is moved into place to accept the next section from the parison that has been cut away from the first mold.

**[0066]** Besides blow molding using continuous extrusion, the forming step may use intermittent extrusion by reciprocating screw systems, ram accumulator-type systems, or accumulator head systems; co-injection stretch blow molding; extruded or co-extruded sheet, blown film tubing, or profiles. Other forming methods include injection molding, thermoforming, vacuum molding, transfer molding, pressure forming, heat-sealing, casting, melt casting, RF welding and so on. For example, a flat film may be cut into a desired shape. Two portions of the flat film may be sealed at the edges to form a bladder. The film may alternatively be rolled into a tube and RF welded at the edges to form a bladder.



**[0067]** The bladder may be inflated with a fluid, preferably a gas, and permanently sealed. The durable, elastomeric membranes of the inflated bladders may be incorporated into the sole of an article of footwear, for example. By “durable” it is meant that the membrane has excellent resistance to fatigue failure, which means that the membrane can undergo repeated flexing and/or deformation and recover without delamination along the layer interfaces of composite barrier membranes, preferably over a broad range of temperatures. Footwear, and in particular shoes, usually include two major components: a shoe upper and a sole. The general purpose of the shoe upper is to snugly and comfortably enclose the foot. Ideally, the shoe upper should be made from an attractive, highly durable, comfortable materials or combination of materials. The shoe upper can be formed from a variety of conventional materials including, but not limited to, leathers, vinyls, nylons, and other generally woven materials. The sole, constructed from a durable material, is designed to provide traction and to protect the foot during use. The sole also typically serves the important function of providing enhanced cushioning and shock absorption during athletic activities to protect the feet, ankles, and legs of the wearer from the considerable forces generated. The force of impact generated during running activities can amount to two or three times the body weight of the wearer, while other athletic activities such as playing basketball may generate forces of between six and ten times the body weight of the wearer. To provide these functions, the sole typically has a midsole or insole having cushioning and an outsole having a traction surface. The bladder preferably is applied to the insole portion of a shoe, which is

generally defined as the portion of the shoe upper directly underlying the plantar surface of the foot. Use of a bladder for cushioning in a shoe is known in the art.

**[0068]** Because of the desirable low haze and high clarity of the membrane containing the nano-filler, the bladder may form at least a part of the exterior of the shoe.

**[0069]** The membranes preferably are capable of containing a captive gas for a relatively long period of time. In a highly preferred embodiment, for example, the membrane should not lose more than about 20% of the initial inflated gas pressure over a period of approximately two years. In other words, products inflated initially to a steady state pressure of between 20.0 to 22.0 psi should retain pressure in the range of about 16.0 to 18.0 psi for at least about two years.

**[0070]** The bladder or cushioning device may be inflated with air or components of air such as nitrogen, or with supergases. When used as cushioning devices in footwear such as shoes, the bladder may be inflated, preferably with nitrogen, to an internal pressure of at least about 3 psi, preferably at least about 5 psi, and up to about 50 psi. Preferably the bladder is inflated to an internal pressure of from about 5 psi to about 35 psi, more preferably from about 5 psi to about 30 psi, still more preferably from about 10 psi to about 30 psi, and yet more preferably from about 10 psi to about 25 psi. It will be appreciated by the skilled artisan that in applications other than footwear applications the desired and preferred pressure ranges may vary dramatically and can be determined by those skilled in that particular field of application.

Accumulator pressures, for example, can range up to perhaps 1000 psi.

Accumulator pressures are preferably up to about 500 psi. A preferred range of pressure for accumulator applications is from about 200 psi to about 1000 psi, but pressures as low as about 25 psi are possible depending upon the design of the accumulator. Typical pressures for bladders used in sports balls are from about 8 to about 40 psi. After being inflated, the inflation port is sealed, for example by RF welding, for a permanently sealed inflated bladder.

**[0071]** For the bladders to remain permanently inflated, the gas transmission rate must be suitably low. In one preferred embodiment, the membrane of the bladder has a gas transmission rate toward the inflationary gas, which is preferably air or nitrogen gas, should be less than about 15 cubic centimeters per square meter per atmosphere per day ( $\text{cc}/\text{m}^2\cdot\text{atm}\cdot\text{day}$ ), preferably less than about  $6 \text{ cc}/\text{m}^2\cdot\text{atm}\cdot\text{day}$ , particularly less than about  $4 \text{ cc}/\text{m}^2\cdot\text{atm}\cdot\text{day}$ , more preferably less than about  $2.5 \text{ cc}/\text{m}^2\cdot\text{atm}\cdot\text{day}$ , yet more preferably less than about  $1.5 \text{ cc}/\text{m}^2\cdot\text{atm}\cdot\text{day}$ , and particularly preferably less than about  $1 \text{ cc}/\text{m}^2\cdot\text{atm}\cdot\text{day}$ . An accepted method of measuring the relative permeance, permeability, and diffusion of different film materials is set forth in the procedure designated as ASTM D-1434. While nitrogen gas is the preferred captive gas for many embodiments and serves as a benchmark for analyzing gas transmission rates in accordance with ASTM D-1434, the membranes can contain a variety of different gases and/or liquids.

**[0072]** Accumulators, and more particularly, hydraulic accumulators are used for vehicle suspension systems, vehicle brake systems, industrial hydraulic

accumulators or for other applications having differential pressures between two potentially dissimilar fluid media. The membrane separates the hydraulic accumulator into two chambers or compartments, one of which contains a gas such as nitrogen and the other one of which contains a liquid.

**[0073]** In addition to use for cushioning devices for footwear and for accumulators, it should be appreciated that the membranes of the present invention have a broad range of applications, including but not limited to bladders for inflatable objects such as balls, including footballs, basketballs, and soccer balls; inner tubes; flexible floatation devices such as tubes or rafts; as a component of medical equipment such as catheter balloons; as part of an article of furniture such as chairs and seats, as part of a bicycle or saddle, as part of protective equipment including shin guards and helmets; as a supporting element for articles of furniture and, more particularly, lumbar supports; as part of a prosthetic or orthopedic device; as a portion of a vehicle tire, particularly the outer layer of the tire; and as part of certain recreation equipment such as components of wheels for in-line or roller skates.

**[0074]** The invention is further described in the following examples. The examples are merely illustrative and do not in any way limit the scope of the invention as described and claimed. All parts are parts by weight unless otherwise noted.

Example 1.

**[0075]** Two single-layer sheets of ethylene-vinyl alcohol copolymer [EVOH] containing 5% by weight of a laminar non-filler are prepared using ETC-

133 from Kuraray/Evalca as the EVOH and Cloisite 15A (a nano-filler clay treated with dimethyl, dihydrogenated tallow, quaternary ammonium chloride) and Cloisite 30A (a nano-filler clay treated with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride) as the filler. These samples were produced in a concentrate then diluted as follows: First, a high clay containing polymer sample was produced via extrusion. Then, the concentrate was re-extruded with the desired amount of polymer to achieve the 5% by weight clay content. The extrudate from this second extrusion was pelletized to produce extruded ETC-133 clay nanocomposite pellets.

**[0076]** The increased barrier properties of the barrier nanocomposite layer was determined as follows. The extruded ETC-133 clay nanocomposite pellets were extruded to produce 1 mil-thick cast film for gas transmission rate measurement. The gas transmission rate measurement was conducted at 20°C and 65% relative humidity in 100% oxygen with nitrogen as carrier gas. The gas transmission rates of the two nanocomposite films were compared to the gas transmission rate of unfilled ETC-133 as reported by the manufacturer. The results are summarized in Table 1.

**[0077]** Table 1. Oxygen transmission rate

Sample	OTR (cc-mil/m <sup>2</sup> - day-atm)
95 wt.% ETC-133/5 wt.% Cloisite 15A	5.16
95 wt.% ETC-133/5 wt.% Cloisite 30A	4.07
ETC-133 (as reported by Kuraray)	5.76

**[0078]** The extruded ETC-133 clay nanocomposite pellets are then co-extruded with a thermoplastic polyurethane to form multi-layer construction membranes and the membranes are formed into sealed bladders and inflated with a gas as described in U.S. Patent 5,952,065. The bladders are incorporated into a sole of a shoe as described in U.S. Patent 5,952,065.

Example 2.

**[0079]** The extruded ETC-133 clay nanocomposite pellets of Example 1 are extruded to form a microlayer polymeric composite according to Example 1 of Bonk et al., U.S. Patent No. 6,082,025, with the extruded ETC-133 clay nanocomposite pellets of Example 1 replacing the LCF 101A material of the patent example. The microlayer polymeric composite is formed into a sealed, inflated bladder, which is then incorporated into a sole of a shoe as described in Example 1.

**[0080]** The invention has been described in detail with reference to preferred embodiments thereof. It should be understood, however, that variations and modifications can be made within the spirit and scope of the invention and of the following claims.